

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re accompanying application of)

A. D. HORTON ET AL)

Filed June 18, 2003)

PROCESS FOR PREPARING STYRENE)

June 20, 2003

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Sir:

CLAIM TO PRIORITY

Applicants reaffirm the claim for the benefit of filing date of the following foreign patent application referred to in Applicants' Declaration:

EP Application Serial No. 02254359.9 - filed June 21, 2002

A copy of the application certified by the European Patent Office is enclosed.

Respectfully submitted,

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Enclosure

1000000

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Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02254359.9

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr.:
Application no.: 02254359.9
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Anmelder/Applicant(s)/Demandeur(s):

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Process for preparing styrene

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PROCESS FOR PREPARING STYRENE

The invention pertains to a process for preparing styrene by catalytically dehydrating 1-phenylethanol in the liquid phase.

Such processes are known in the art, for example from
5 US 3,526,674 wherein the dehydration of α -phenylethanol (1-phenyl ethanol) is described to form styrene in the liquid phase at temperatures above 200 °C. This process also provides considerable amounts of ethyl benzene-like byproducts that are distilled off. Such distillation
10 process is expensive because the boiling points of product and byproduct are close. Further, apart from relatively low-boiling ethyl benzene byproduct also oligomers and polymers are formed that are generally indicated as heavy condensation products or "heavies."
15 More recently, US 5,639,928 disclosed a process for suppressing such undesirable heavy formation when making styrene monomer by catalytically dehydrating 1-phenyl ethanol. It was found that residue formation is suppressed by performing the reaction in the presence of
20 a nitro group-containing additive.

The synthesis of styrene is important because this product functions as starting material for valuable commercial products such as plastics and the like. The above disadvantages of these processes contribute
25 considerably to the cost price of the styrene starting material. These costs-enhancing effects not only arise from the quantities of byproducts obtained, but also from the properties thereof. Particularly, viscous high-

molecular byproducts contribute substantially to the purification costs, whereas low-viscous low-molecular byproducts are much easier to remove.

It is therefore an object of the present invention to provide in a new process resulting in byproducts that are less viscous and have lower molecular weight than the byproduct obtained with the processes of the prior art.

It was now found that low viscous byproducts having relatively low molecular weight are obtained when a chain transfer agent is present in the reaction mixture to be dehydrated. Thus the invention pertains to the process for preparing styrene by catalytically dehydrating 1-phenylethanol in the liquid phase, wherein the process is performed in the presence of at least 0.1 wt.% of a chain transfer agent. It is stressed that the amount of heavies obtained is not necessarily decreased, but the improvement is particularly found in the decreased viscosity and molecular weight thereof.

Dehydration conditions of temperature and pressure as well as the selection of the catalyst are generally known in the field. Such procedure generally involves dehydrating 1-phenylethanol in the liquid phase at temperatures ranging from about 150 to about 350 °C, preferably from about 180 to about 280 °C, and more preferably from about 200 to 260 °C. The pressure generally is sub-atmospheric to atmospheric, from about 0.05 to about 1 bar, preferably from about 0.2 to about 0.6 bar, and more preferably from about 0.3 to about 0.5 bar.

Acidic type catalysts are preferably employed such as aliphatic and aromatic sulfonic acids. Examples are oxalic acid, sulphuric acid, and particularly p-toluene sulfonic acid.

An essential feature of the present invention is the use of at least 0.1 wt.% of a chain transfer agent. The usual chain transfer agents can be employed, such as those disclosed in the reference work by K.C. Berger and G. Brandrup, Polymer Handbook (ed. J. Brandrup and E.H. Immergut; 3rd ed. John Wiley & Sons), Transfer Constants to Monomer, Polymer, catalyst, Solvent, and Additive in Free Radical Polymerization, II, pp. 81-151. Particularly useful CHAIN TRANSFER AGENT's are selected from phenol, methylphenol, ethylphenol, benzaldehyde, benzylalcohol and benzoic acid or esters thereof. Of course, also mixtures of at least two different chain transfer agents can be used. In practice the amount of chain transfer agent used is generally between about 0.1 and about 10 wt.%. Preferred amounts of chain transfer agent range between about 0.3 and about 5 wt.%, most preferably between about 0.8 and about 1.5 wt.%.

An interesting embodiment of the invention is to use the crude product of the above reaction as a source of the chain transfer agent. In a commonly used process for preparing 1-phenylethanol, ethyl benzene is first oxidized with air to form ethylbenzene hydroperoxide. This is then reacted with propene to yield propylene oxide and 1-phenylethanol ((K. Weissermel and H-J Arpe, Industrial Organic Chemistry, Third edition (1997) VCH Verlagsgesellschaft GmbH, pp. 267-270). In this process, small amounts of compounds such as benzylaldehyde, benzylalcohol, phenol, and ethylphenols are formed as a byproduct. Thus the crude 1-phenylethanol stream as such contains amounts of chain transfer agent as the result of a side-reaction. In a conventional process, process steps are carried out to remove these components. For example, phenol is removed by a caustic wash or distillation

(US 5,538,599) and benzaldehyde is removed by distillation. These separation steps may now fully or partially be omitted and (part of) the product stream of the dehydration reaction may be used as the source of chain transfer agent by recycling such product stream to the reactor. The concentration of chain transfer agent in the feed to the dehydration reaction is hereby increased. Thus only at the start of such process highly viscous byproduct are formed, which is insignificant since these minor amounts are of no influence on the end viscosity after the recycling process has set forth. It is also possible to start with the addition of a chain transfer agent, performing the process and then replacing the addition of the chain transfer agent by addition of (part of) the product stream. A method of continuously adding both external chain transfer agent and recycled product stream is also possible. The invention thus further pertains to a process for preparing styrene comprising the steps:

- a) catalytically dehydrating a feed comprising 1-phenylethanol in the liquid phase in a reactor to obtain a product stream comprising chain transfer agent; and
- b) recycling at least part of the chain transfer agent-containing product stream to the reactor to be combined with the feed.

In this manner at least 0.1 wt.% of the chain transfer agent is added to the feed.

The new process has many advantages over the existing processes since the low viscosity byproducts allow easy handling procedures, wherein the reaction mass is much more easily pumped through the plant. Further, the low viscosity byproducts have better heat exchange

properties, requiring cheaper heat exchangers and the like. In the case when recycle of dehydration reaction product is used to increase the level of chain transfer agent in the feed, the process has the further advantage that some expensive separation steps are no longer necessary.

The invention is further illustrated by the following non-limiting examples.

Example 1

A dehydration reaction of 1-phenylethanol was carried out as follows. 64 g of heavy residue from a previous dehydration reaction was placed in a reactor. A mixture of 99 wt.% 1-phenylethanol (laboratory grade) and 1 wt.% phenol was continuously fed to the reactor at a rate of 30 g/h. The reactor conditions were 0.6 bar and 225 °C. The feed contained 200 mg p-toluene sulfonic acid/kg feed. Reaction products styrene and water were removed as vapour. After 48 h operation, a total of 195 g of heavy residue was present. Average molecular weight of this residue was determined as follows: A solution of the sample was prepared by adding about 3 ml of THF (tetrahydrofuran) (containing 0.1% of elemental sulphur as internal standard) to 10-15 mg heavy ends at 25 °C and agitating the mixture for 30 min. The samples, together with the reference sample (polystyrene), were then analyzed under the following chromatographic conditions:

Column: PL-Gel, four 30 cm columns (10000, 1000, 100 and 50 Angstroms), 50 µm

Eluent: tetrahydrofuran

Flow rate: 0.8 ml/min

Temperature: 40 °C

Detector: Refractive index (at 30 °C)

Calibration: Polystyrene standard (266-377400 Da)

Molecular weight of the heavy residue was as follows:
Mn 288, Mw 509, Mz 982.

Comparative Example 1

5 A dehydration reaction of 1-phenylethanol was carried
out as in Example 1, except that the feed was only
1-phenylethanol (laboratory grade). 70 g of heavy residue
were charged to the reactor. After 52 h operation a total
of 203 g of heavy residue was present. Molecular weight
of the heavy residue was as follows: Mn 404, Mw 6965,
10 Mz 219513.

Example 2

A dehydration reaction of 1-phenylethanol was carried
out as in Example 1, except that the feed was a mixture
of 99 wt.% of 1-phenylethanol (laboratory grade) and
15 1 wt.% of benzylalcohol. 62 g of heavy residue were
charged to the reactor. After 75 h operation a total of
341 g of heavy residue was present. Molecular weight of
the heavy residue was as follows: Mn 420, Mw 711,
Mz 1165.

C L A I M S

1. A process for preparing styrene by catalytically dehydrating 1-phenylethanol in the liquid phase, characterized in that the process is performed in the presence of at least 0.1 wt.% of a chain transfer agent.
- 5 2. The process according to claim 1 wherein the chain transfer agent is selected from phenol, methylphenol, ethylphenol, benzaldehyde, benzylalcohol and benzoic acid or esters thereof.
3. The process according to claim 1 or 2 wherein the
10 process is performed in the presence of an acidic catalyst.
4. The process according to claim 3 wherein the catalyst is an aliphatic or aromatic sulfonic acid, more preferably p-toluenesulfonic acid.
- 15 5. The process according to any one of the preceding claims wherein the process is performed at 150 to 350 °C.
6. A process for preparing styrene comprising the steps:
 - a) catalytically dehydrating a feed comprising
1-phenylethanol in the liquid phase in a reactor to
20 obtain a product stream comprising chain transfer agent;
and
 - b) recycling at least part of the chain transfer agent-containing product stream to the reactor to be combined with the feed.

A B S T R A C T

PROCESS FOR PREPARING STYRENE

The invention pertains to a process for preparing styrene by catalytically dehydrating 1-phenylethanol in the liquid phase, characterized in that the process is performed in the presence of at least 0.1 wt.% of a chain transfer agent. As an alternative the process is performed by recycling at least part of the chain transfer-containing product stream to the reactor and combining with the feed for preparing the products.

